

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |    |  |                         |
|--|----|--|-------------------------|
| (51) International Patent Classification 6 : | A1 | (11) International Publication Number: | WO 95/17479             |
| C09D 5/29, 5/36, C09C 1/00, B05D 5/06        |    | (43) International Publication Date:   | 29 June 1995 (29.06.95) |

|   |  |   |
|---|--|---|
| (21) International Application Number:                | PCT/US94/13889   | (81) Designated States: BR, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).   |
| (22) International Filing Date:                       | 5 December 1994 (05.12.94)   |   |
| (30) Priority Data:                                   | 08/173,592 23 December 1993 (23.12.93) US  | <b>Published</b><br><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (71) Applicant (for all designated States except US): | BASF CORPORATION [US/US]; Patent Dept., Legal, 26701 Telegraph Road, Southfield, MI 48086-5009 (US).             |   |
| (72) Inventor; and                                    |  |   |
| (75) Inventor/Applicant (for US only):                | JOHNSON, Daniel, W. [US/US]; 35154 University, Westland, MI 48185 (US).  |   |
| (74) Agent:   | MARSHALL, Paul, L.; BASF Corporation, Patent Dept., Legal, 26701 Telegraph Road, Southfield, MI 48086-5009 (US). |   |

(54) Title: COATING COMPOSITION CONTAINING OPTICALLY-VARIABLE PIGMENT AND BLACK PIGMENT

(57) Abstract

A coating composition is described comprising a polymer resin binder and optically variable thin film pigment flakes. The pigment flakes have a multilayer thin film interference structure comprising a metal reflector layer having first and second parallel planar surfaces and, disposed on at least one of said first and second planar surfaces, at least one transparent dielectric layer. The coating composition further comprises a black pigment. This coating composition can be used to prepare a variety of coatings, especially color-plus-clear composite coatings such as those used in the automotive industry.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |  |    |                          |
|----|--------------------------|----|--|----|--------------------------|
| AT | Austria                  | GB | United Kingdom                           | MR | Mauritania               |
| AU | Australia                | GE | Georgia                                  | MW | Malawi                   |
| BB | Barbados                 | GN | Guinea                                   | NE | Niger                    |
| BE | Belgium                  | GR | Greece                                   | NL | Netherlands              |
| BF | Burkina Faso             | HU | Hungary                                  | NO | Norway                   |
| BG | Bulgaria                 | IE | Ireland                                  | NZ | New Zealand              |
| BJ | Benin                    | IT | Italy                                    | PL | Poland                   |
| BR | Brazil                   | JP | Japan                                    | PT | Portugal                 |
| BY | Belarus                  | KE | Kenya                                    | RO | Romania                  |
| CA | Canada                   | KG | Kyrgyzstan                               | RU | Russian Federation       |
| CF | Central African Republic | KP | Democratic People's Republic<br>of Korea | SD | Sudan                    |
| CG | Congo                    | KR | Republic of Korea                        | SE | Sweden                   |
| CH | Switzerland              | KZ | Kazakhstan                               | SI | Slovenia                 |
| CI | Côte d'Ivoire            | LI | Liechtenstein                            | SK | Slovakia                 |
| CM | Cameroon                 | LK | Sri Lanka                                | SN | Senegal                  |
| CN | China                    | LU | Luxembourg                               | TD | Chad                     |
| CS | Czechoslovakia           | LV | Latvia                                   | TG | Togo                     |
| CZ | Czech Republic           | MC | Monaco                                   | TJ | Tajikistan               |
| DE | Germany                  | MD | Republic of Moldova                      | TT | Trinidad and Tobago      |
| DK | Denmark                  | MG | Madagascar                               | UA | Ukraine                  |
| ES | Spain                    | ML | Mali                                     | US | United States of America |
| FI | Finland                  | MN | Mongolia                                 | UZ | Uzbekistan               |
| FR | France                   |    |  | VN | Viet Nam                 |
| GA | Gabon                    |    |  |    |                          |

-1-

COATING COMPOSITION CONTAINING  
OPTICALLY-VARIABLE PIGMENT AND BLACK PIGMENT

Field of the Invention

This invention relates to coating compositions,  
5 and in particular to pigmented coating compositions  
useful for color-plus-clear composite coatings.

Background of the Invention

Optically-variable thin-film pigment flakes  
have been described in the art for a variety of  
10 applications, such as inks for counterfeit-proof  
applications such as currency, and generically for  
coating compositions. They are described, for example,  
in U.S. Patents 4,434,010, 4,704,356, 4,779,898,  
4,838,648, 4,930,866, 5,059,245, 5,135,812, 5,171,363,  
15 and 5,214,530. These pigments are prepared by depositing  
inorganic transparent dielectric layers, semi-transparent  
metal layers, and metal reflecting layers onto a flexible  
web, and separating the layers from the web in such a  
manner as to fragment the deposited thin film layer  
20 structure into pigment particles. These particles are in  
the form of irregularly-shaped flat pigment flakes.  
These pigments are capable of producing dramatic visual  
effects, including dichroic effects not observed in other  
types of pigments.

In many cases, due to cost or other  
considerations such as aesthetics, the optimal level of  
the optically-variable thin-film pigment in a coating  
composition may not be sufficient to provide adequate  
hiding. It is therefore an object of the present  
30 invention to provide coating compositions that have good  
hiding power with low levels of optically-variable thin-  
film pigments, without significantly altering the nature  
of the visual effect provided by the optically-variable  
pigment.

35 Summary of the Invention

According to the present invention, there is  
provided a coating composition comprising a polymer resin

binder and optically variable thin film pigment flakes. The pigment flakes have a multilayer thin film interference structure comprising a metal reflector layer having first and second parallel planar surfaces and, disposed on at least one of said first and second planar surfaces, at least one transparent dielectric layer. The coating composition further comprises a black pigment. This coating composition can be used to prepare a variety of coatings, especially color-plus-clear composite coatings such as those used in the automotive industry.

10 Description of the Preferred Embodiments

Optically-variable thin-film pigment flakes are well-known in the art. Their characteristics and their preparation is described in U.S. Patents 4,434,010, 4,704,356, 4,779,898, 4,838,648, 4,930,866, 5,059,245, 5,135,812, 5,171,363, and 5,214,530, the disclosures of which are incorporated herein by reference in their entirety.

Optically-variable thin-film pigment flakes are prepared by depositing onto a flexible web combinations of transparent dielectric layers, semi-opaque metal layers, and metal reflecting layers to form a multilayer thin film interference structure. The interference structure typically has at least one metal reflecting layer and at least one transparent dielectric layer. Various combinations of these layers can be utilized to achieve the desired optically variable effect. In a preferred embodiment, the interference structure produces a dichroic optical effect and has in order, on one side of the metal reflecting layer, at least one transparent dielectric layer and at least one semi-opaque metal layer. In a particularly preferred embodiment, this layer structure is symmetrical on both sides of the metal reflecting layer.

35 Aluminum is often used as the metal reflecting layer for a variety of reasons such as its cost and

commercial availability, although other materials, such as gold, copper, or silver can also be used. The semi-opaque metal layer can be formed from metals such as chromium, nickel, or Inconel. The transparent dielectric layers can be formed from materials such as silicon dioxide, magnesium fluoride, or aluminum oxide. Layer thicknesses can be varied according to the particular desired characteristics of the pigment. For example, U.S. 5,135,812 describes useful thicknesses being on the order of 80 nm for the metal reflecting layer, 5 nm for the semi-opaque metal layers, and thicknesses of a plurality of halfwaves of the particular design wavelength for the transparent dielectric layers.

As mentioned above, the optically-variable thin-film pigment flakes are prepared by coating the semi-opaque metal layers, transparent dielectric layers, and metal reflecting layer onto a flexible web, and separating the web from the multilayer structure to form the pigment flakes. The web is typically a polymer material, such as polyvinyl alcohol or polyethyleneterephthalate. The separation can be accomplished by stripping the multilayer structure from the web, in which case a stripping layer, as is known in the art, is preferably deposited onto the web prior to the other layers. Heat and/or solvent may be used to facilitate the stripping process. Alternatively, the web may be dissolved in a suitable solvent (aqueous or organic, depending on the solubility of the web material) to accomplish the separation. The coated web may optionally be cut or shredded to more easily fit into a container prior to the dissolution step.

As the multilayer structure is separated from the web, it typically breaks into flakes of irregular shapes and sizes. These flakes will usually require further processing to achieve the size requirements of the present invention. This can be accomplished by

techniques known in the art, such as ultrasonic agitation, milling, or grinding. It may be preferred to use various combinations of solvents, surfactants, and/or resins during the size reduction process, as is known in  
5 the art.

In a preferred embodiment, the above-described techniques are used to achieve the desired average particle size of 5 to 40  $\mu\text{m}$  and the desired particle size distribution where no more than 10% of the particles have  
10 a particle size of greater than 50  $\mu\text{m}$  and substantially none of the particles have a particle size of greater than 125  $\mu\text{m}$ , as described in the U.S. patent application  
15 entitled "Coating Composition Containing Optically-Variable Pigment", filed on even date herewith in the names of Kendall Scott and Daniel W. Johnson. It may, however, be necessary to use microscopic filtering techniques, as is known in the art, to assure that the  
desired particle size distribution is achieved.

The black pigment used according to the present invention can be any pigment that absorbs virtually all visible light across the visible spectrum. Such pigments are identified on the Color Index as C.I. Pigment Black, and include graphite pigments, carbon black pigments, black iron oxide pigments, and the like. In a preferred embodiment, the black pigment is a carbon black or an iron oxide pigment. These pigments are preferred for their hiding power. Some slight variance from a pure black pigment is permitted, as long as it does not significantly detract from the optically-variable effect of the optically-variable thin-film pigment in the coating composition. For example, Graphitan<sup>®</sup> has a slight chalky-gray tint, but still absorbs sufficiently across the visible spectrum to provide the desired effect. Examples of useful black pigments include  
30 Monarch<sup>®</sup> 900 (from Cabot), B.P. 1300 (from Cabot), Graphitan<sup>®</sup> 7525 (from Ciba-Geigy), FW 200 (from De  
35

Gusson), Raven® 450 (from Columbian), #3 Lampblack (from General Carbon), and Raven® #14 (from Columbian). The black pigment can be present at levels of 0-90% by weight of the total pigment in the composition, and is preferably present at levels of 3-40%.

According to the invention, the combination of optically-variable thin-film pigment and the black pigment is used in a coating composition along with a binder resin. Useful pigment:binder ratios range from 0.03:1 to 0.2:1, and preferably 0.05:1 to 0.15:1. The binder used in the present invention may be selected from of any of a number of polymers known in the art. Polymers known in the art to be useful in coating compositions include acrylics, vinyls, polyurethanes, polycarbonates, polyesters, alkyds, epoxy resins, and polysiloxanes. Preferred polymers include acrylics and polyurethanes. The resin may be of the thermoplastic type, but are preferably crosslinkable, and thus comprise one or more type of cross-linkable functional groups. Such groups include, for example, hydroxy, isocyanate, amine, epoxy, acrylate, vinyl, silane, and acetoacetate groups. These groups may be masked or blocked in such a way so that they are unblocked and available for the cross-linking reaction under the desired curing conditions, generally elevated temperatures (i.e., thermoset). Useful cross-linkable functional groups include hydroxy, epoxy, acid, anhydride, silane, and acetoacetate groups. Preferred cross-linkable functional groups include hydroxy functional groups and amino functional groups.

The above-described polymers may be self-cross-linkable, or the coating composition may include a separate cross-linking agent that is reactive with the functional groups of the polymer. When the polymer comprises hydroxy functional groups, for example, the cross-linking agent may be an aminoplast resin,

isocyanate and blocked isocyanates (including isocyanurates), and acid or anhydride functional crosslinking agents.

The coating composition of the present invention may be solvent-borne or water-borne. Suitable binder resins for water-borne coating compositions are water-dispersible or water-soluble ionic or nonionic resins. Anionic or nonionic resins are preferred for use in topcoat applications. Examples of water-dispersible polymers used for topcoats are contained in US Patent Nos. 4,794,147; 4,791,168; and 4,518,724, all of which are incorporated herein by reference. Such systems may also include a crosslinker, as described above. Polymeric-type melamine crosslinkers are often preferred for water-borne coating compositions where the binder resin is anionically stabilized, as such polymeric-type melamines do not require strong acid catalysis. When the film-forming resin is nonionically stabilized, a polymeric melamine may be used or a monomeric melamine may be used in conjunction with a strong acid catalyst like a sulfonic acid or blocked sulfonic acid.

A solvent may optionally be utilized in the coating composition of the present invention. Although the composition of the present invention may be utilized, for example, in the form of substantially solid powder, or a dispersion, it is usually preferred that the composition is in a substantially liquid state, which can be accomplished with the use of a solvent. This solvent should act as a solvent with respect to both the binder resin as well as any crosslinking agents used. In general, as is well-known in the art, depending on the solubility characteristics of the components in the coating composition, the solvent can be any of a number of organic solvent(s) and/or water. In one preferred embodiment, the solvent is a polar organic solvent. More preferably, the solvent is a polar aliphatic solvents or

5 polar aromatic solvents, such as a ketone, ester, acetate, aprotic amide, aprotic sulfoxide, or aprotic amine. Examples of useful solvents include methyl ethyl ketone, methyl isobutyl ketone, m-amyl acetate, ethylene glycol butyl ether-acetate, propylene glycol monomethyl ether acetate, xylene, n-methylpyrrolidone, or blends of aromatic hydrocarbons.

10 In another preferred embodiment, the solvent is water or a mixture of water with small amounts of aqueous co-solvents. Preferred co-solvents include acetates such as butyl acetate, hexyl acetate, and octyl acetate; glycol ethers and glycol ether acetates, such as propylene glycol ether and propylene glycol monomethyl ether acetate; and ketones, such as methyl propyl ketone, methyl isobutyl ketone, and methyl hexyl ketone. Glycol ethers and glycol ether acetates are especially preferred.

15 For most liquid coating compositions, the solvent may be present in an amount of from about 0.01 weight percent to about 99 weight percent, preferably from about 10 weight percent to about 60 weight percent, and more preferably from about 30 weight percent to about 50 weight percent.

20 It may be desirable to include small amount of rheology control agents, for example fumed silicas, hectorite clays, bentonite clays, or cellulosics like cellulose acetate butyrate. Such materials are usually used at levels of less than 10% based on the total solid weight of reactants. Rheology control agents are used to control the flow and levelling of the composition during application and curing steps. The rheology control agent is also useful for controlling the metallic appearance of the coating. Such materials may help "fix" the pigment flake surface in an alignment parallel to the surface of the coating to maximize the brightness when viewed head-on and to maximize the darkness when viewed obliquely.

The coating composition of the invention may further comprise additional pigment(s). In one preferred embodiment, the coating composition of the invention further comprises a metallic pigment, as described in the 5 U.S. patent application entitled "Coating Composition Containing Optically-Variable Pigment and Metallic Pigment", filed on even date herewith in the name of Daniel W. Johnson. In another preferred embodiment, the optically-variable thin-film pigment is a dichroic 10 pigment, and the coating composition further comprises an interference mica in one of the colors of the optically-variable thin-film pigment, as described in the U.S. patent application entitled "Coating Composition Containing Optically-Variable Dichroic Pigment and 15 Interference Mica Pigment", filed on even date herewith in the name of Daniel W. Johnson. The coating composition may also contain a transparent pigment to operate in a subtractive mode to modify the colors or block unwanted colors of the optically-variable thin-film 20 pigment. For example, in the case of a gold-to-green shifting pigment, the addition of yellow dyes or transparent yellow pigments blocks the blue reflective light at large viewing angles by absorbing the undesired colors. Combinations of any of the above-described 25 supplementary pigments with each other or with other known pigments may also be made.

The coating compositions according to the invention can contain optional ingredients such as wetting agents, surfactants, defoamers, antioxidants, UV 30 absorbers, light stabilizers, plasticizers, and so forth. Examples of surfactants and wetting agents include alkyl imidazolines such as those available from Ciba-Geigy Industrial Chemicals as Amine C®, acetylenic alcohols available from Air Products and Chemicals as Surfynol® 35 104. These optional ingredients, when present,

constitute from about 0 to 20 percent by weight of resin solids.

5       The prepared coating composition is applied to a substrate by any of a number of conventional means, for example by spraying, brushing, dipping or flowing. The preferred methods of application are by spraying or electrostatic spraying. These methods are widely used, especially in the application of automotive coatings. For example, the coating may be applied using a Model 62 10 syphon spray gun (available from Binks Manufacturing Corp., Franklin Park, Ill.) with 50-80 psi atomizing air pressure.

15       The substrate to which the coating composition of this invention is to be applied may be, for example, metal, ceramic, plastic, glass, paper, or wood. The substrate may also be any of the aforementioned materials precoated with this or another coating composition. The 20 coating compositions of this invention have been found to be particularly useful over precoated steel or plastic substrates in automotive applications. They are particularly suited to use over primed automotive substrates as topcoat formulations or basecoat 25 formulations that are overcoated with clearcoat formulations.

30       After application of the coating composition to the substrate, the coating is cured, preferably by heating at a temperature and for a length of time sufficient to cause the conversion of all or nearly all of the reactive groups. The cure temperature is usually from 115°C to 180°C, and the length of cure is usually 15 minutes to 60 minutes. Preferably, the coating is cured at 120-150°C for 20 to 30 minutes. The thickness of the 35 cured coating can be from 1 to 150 microns, but when used as an automotive topcoat or basecoat the coating thickness is generally from 10 to 70 microns.

In a particularly preferred embodiment, the composition of the invention is used as the pigmented basecoat of a composite color-plus-clear coating. Such composite coatings are popular for their depth of color and liquid glossy surface appearance. They have found 5 particularly wide acceptance in the field of automotive coatings. The basecoat may be cured before the clearcoat is applied or the basecoat may be given a wet-on-wet application of a clearcoat. By the term "wet-on-wet" it 10 is meant that after application the basecoat is allowed to flash, or dry, to remove most of the water and other solvent that it contained, but it is not cured before the clearcoat composition is applied. After the clearcoat composition is applied, it is allowed to flash or dry for 15 a period of time, then the basecoat and the clearcoat are cured together.

The clearcoat may be a coating composition according to this invention or another composition known to the art to have utility as a clearcoat. The clearcoat does not necessarily need to use the cure mechanism used 20 by the basecoat, although the cure mechanisms used must not interfere with one another.

The basecoat may be applied in one or two layers, with a short period between application of layers 25 to allow solvent and water to evaporate (termed a "flash" period). After application, the basecoat may be further dried, preferably at a slightly elevated temperature, as in a 120°F oven, for a period of 5 to 20 minutes before the clear coat composition is applied. The clearcoat composition is preferably applied by spraying, in one 30 layer, or preferably two layers with a short flash between layers. The clearcoat composition is allowed to flash under ambient or heated conditions for 1-20 minutes. The uncured coatings are then cured, usually by 35 thermoset methods as described hereinabove. The

resulting appearance and physical properties are excellent.

The invention is further described by the following examples.

5      Example 1

A coating composition was prepared having the following formulation:

Resin Vehicle Containing:

18.01% acrylic microgel  
35.00% melamine resin crosslinker  
46.99% OH-functional acrylic resin binder  
(56.08 parts by weight total vehicle)

5

solids per  
100 parts by weight paint)

Pigment Containing:

80% optically-variable thin-film pigment flakes  
10 20 carbon black pigment  
(4.47 parts by weight total pigment per 100

parts

by weight paint)

Additives:

15 polybutyl acrylate 0.20 parts/100 parts paint  
Tinuvin® 1130 0.50% (based on vehicle  
solids)  
Nacure® 5225 0.50% (based on vehicle  
solids)  
20 methanol 3.0 parts/100 parts paint

The coating compositions were reduced to 17" #4 Ford Cup with n-butyl acetate, and sprayed onto a primed metal panel, flash dried, and overcoated with a clearcoat containing an OH-functional acrylic resin and a melamine resin crosslinker. The coatings were then baked for 30 minutes at 121°C to cure to a hard durable coating having a basecoat thickness of 15-20 µm and a clearcoat thickness of 41-46 µm. For comparison, an identical panel was prepared, except that the pigment was composed of 100% of the optically-variable thin-film pigment. The panel prepared according to the invention provided a darker color while exhibiting a dichroic effect that was as strong or stronger than the comparison panel.

35 The invention has been described in detail with reference to particular embodiments thereof. It is

understood that modifications and variations may be made within the spirit and scope of the invention.

## WHAT IS CLAIMED IS:

1. A coating composition comprising a polymer resin binder and optically variable thin film pigment flakes, said pigment flakes having a multilayer thin film interference structure comprising a metal reflector layer having first and second parallel planar surfaces, and, disposed on at least one of said first and second planar surfaces, at least one transparent dielectric layer, said coating composition further comprising a black pigment.
- 10 2. A coating composition according to claim 1 wherein the multilayer thin film interference structure comprises, disposed on both of said first and second planar surfaces, at least one transparent dielectric layer.
- 15 3. A coating composition according to claim 1 wherein the multilayer thin film interference structure further comprises, disposed on at least one of said first and second planar surfaces, at least one semi-opaque metal layer.
- 20 4. A coating composition according to claim 2 wherein the multilayer thin film interference structure further comprises, disposed on both of said first and second planar surfaces, at least one semi-opaque metal layer.
- 25 5. A coating composition according to claim 4 wherein the layer configuration on each side of said first and second planar surfaces are symmetrical with each other.
- 30 6. A coating composition according to claim 4 wherein the multilayer thin film interference structure comprises at least one transparent dielectric layer having an index of refraction of 1.65 or less.
- 35 7. A coating composition according to claim 1 wherein the multilayer thin film interference structure comprises at least one transparent dielectric layer having an index of refraction of 1.65 or less.

8. A coating composition according to claim 1 wherein the optically variable thin film pigment flakes are prepared by coating the layers of the multilayer thin film interference structure onto a flexible web, separating the web from the multilayer coating so as to produce flakes of the multilayer thin film interference structure, and processing the flakes if necessary to provide said average particle size and particle size distribution.

10 9. A coating composition according to claim 1 wherein said black pigment is a carbon black pigment or an iron oxide pigment.

15 10. A coating composition according to claim 1 wherein the black pigment is present in an amount of 3 to 40%, based on total pigment weight.

11. A coating composition according to claim 1 wherein said combination of optically-variable pigment and said black pigment, and said binder are present in a pigment:binder ratio of from 0.03:1 to 0.20:1.

20 12. A coating comprising a substrate having thereon a layer of the coating composition according to claim 1.

25 13. A coating according to claim 12 wherein said layer of the coating composition is the colored layer of a color-plus-clear composite coating.

14. A coating according to claim 12 wherein the substrate is an automotive body panel.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/13889

**A. CLASSIFICATION OF SUBJECT MATTER**

|       |          |          |          |          |
|-------|----------|----------|----------|----------|
| IPC 6 | C09D5/29 | C09D5/36 | C09C1/00 | B05D5/06 |
|-------|----------|----------|----------|----------|

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

|       |      |      |
|-------|------|------|
| IPC 6 | C09D | C09C |
|-------|------|------|

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|----------|---|-----------------------|
| X        | EP,A,0 493 981 (NIPPON PAINT CO.) 8 July 1992<br>see page 2, line 55 - page 3, line 5<br>see page 3, line 28 - line 32<br>see page 3, line 46 - line 57<br>see page 4, paragraph 2<br>see page 4, line 35 - line 36<br>---<br>EP,A,0 571 836 (BASF) 1 December 1993<br>see abstract<br>see column 3, line 35 - line 58<br>see column 7, line 54 - line 56<br>see column 8, line 13 - line 18<br>---<br>-/-/ | 1,9-12,<br>14         |
| A        |   | 1,3,12,<br>14         |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

|   |  |
|---|--|
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 29 March 1995   | 27.04.95   |

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+ 31-70) 340-3016

Authorized officer

Girard, Y

**INTERNATIONAL SEARCH REPORT**

International Application No

PCT/US 94/13889

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|----------|---|-----------------------|
| A        | US,A,4 434 010 (GARY S. ASH) 28 February<br>1984<br>cited in the application<br>see column 7, line 64 - column 8, line 28;<br>figure 4<br>---                 | 1,8                   |
| A        | PATENT ABSTRACTS OF JAPAN<br>vol. 014, no. 208 (C-0714) 27 April 1990<br>& JP,A,02 045 578 (NIPPON PAINT CO LTD) 15<br>February 1990<br>see abstract<br>----- | 1-14                  |

**INTERNATIONAL SEARCH REPORT**

International Application No

PCT/US 94/13889

| Patent document cited in search report | Publication date | Patent family member(s) |         | Publication date |
|--|------------------|-------------------------|---------|------------------|
| EP-A-0493981                           | 08-07-92         | JP-A-                   | 5179174 | 20-07-93         |
| EP-A-0571836                           | 01-12-93         | DE-A-                   | 4217511 | 02-12-93         |
|  |                  | JP-A-                   | 6032994 | 08-02-94         |
|  |                  | US-A-                   | 5364467 | 15-11-94         |
| US-A-4434010                           | 28-02-84         | US-A-                   | 5383995 | 24-01-95         |
|  |                  | US-A-                   | 5171363 | 15-12-92         |
|  |                  | US-A-                   | 5281480 | 25-01-94         |
|  |                  | US-A-                   | 5279657 | 18-01-94         |
|  |                  | US-A-                   | 5059245 | 22-10-91         |
|  |                  | US-A-                   | 5084351 | 28-01-92         |
|  |                  | US-A-                   | 5135812 | 04-08-92         |